# Electrons on the double helix: optical experiments on native DNA

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Optical experiments on calf thymus DNA films subjected to different buffer environments are reported. The optical conductivity is that of a disordered or lightly doped semiconductor with a well-defined band-gap for charge excitations and low frequency transport determined by a small number of strongly localized electron states.

The question whether electrons are delocalized along the DNA duplex has attracted substantial recent interest and controversy. Both short and long-range migration was found by studies that were chemical in nature [1]. DC conductivity measurements on single DNA strands led to equally controversial results - with metallic [2], semiconducting [3] and insulating [4,5] behavior all observed. Recent experiments [6] are also suggestive of a proximity-induced superconductivity at low temperatures. DNA networks in contrast were found to be highly resistive [7]. Our earlier experiments [8] conducted on λ-DNA in the microwave spectral range gave evidence for a large resistance associated with the duplex and for a thermally driven transport process.

These conflicting results may, to a large extent be due to different DNA varieties. A native DNA duplex with random (or nearly random) base pair sequences is expected to have electron states that are different than an oligomer with identical base pairs, such as a poly(C)-poly(G) track. In addition, the DNA configuration is sensitive to the buffer environment, which surrounds the duplex. In a dry form the duplex has non-parallel base pairs, and at higher water concentrations the duplex undergoes a structural change to a more ordered system [9]. This then may lead to widely different transport properties and also charge excitations of a different nature.

In order to examine the nature of electron states in native DNA, we have conducted optical measurements spanning a wide spectral range, from microwave frequencies to the UV part of the electromagnetic spectrum, on oriented films, fabricated from DNA extracted from calf thymus. Our findings concerning the vibrational modes will be discussed elsewhere. Here we focus on the electronic excitations at high and at low energies. Our data gives evidence for well-defined charge excitations at high energies involving the p-orbitals of the base pairs, and at low energies charge excitations displaying all the characteristics of conduction due to a small number of localized electron states. Thus our experiments suggest that DNA is a wide bandgap semiconductor, with intrinsic disorder, counterion fluctuations, and possibly other sources leading to a small number of localized electronic states on the base pair sequence.

Wet-spun, free-standing oriented samples were prepared from calf thymus Li-DNA (Pharmacia) with a molecular weight of $10^7$ (corresponding to contour length of 5 mm or some 100 persistence lengths) by a method described by Rupprecht et al [10]. This spinning allows controlled production of sufficient amounts of highly oriented thin films by spooling DNA fibers that are continuously stretched during precipitation into an aqueous alcohol solution. Films of thickness of 0.2 mm and lateral dimensions between 5 and 10 mm were used.

In all applicable cases placing it in a chamber with appropriate relative humidity controlled the hydration of the DNA sample. Several configurations were employed to evaluate the optical conductivity $\sigma_1(\omega)$. In all cases we treat the collection of DNA strands as a collection of thin wires, of diameter 2 nm, and we define the conductivity $\sigma$ as $j/E$ where $j$ is the electric current density induced along the helix axis. For randomly coiled DNA strands the loss due to motion of electric charges $W$ is, to a good approximation, given by $W = \frac{1}{3} V \sigma (E_0)^2$, where $V$ is the volume of the sample and $E_0$ is the time averaged applied ac field at the position of the sample. At 12 GHz the conductivity was evaluated from the measured loss of highly sensitive resonant cavities that were loaded with the material. The technique and the analysis, which leads to evaluation of the conductivity from the measured losses, is well established [11]. In the millimeter spectral range, 100 GHz to 1000 GHz, backward wave oscillators were employed as coherent sources in a transmission con-

figuration [12]. The oriented calf-thymus DNA film was placed on a 1 mm thick sapphire substrate and then held in place by a sheet of 6 $\mu$m thick mylar to form a three layer system. Transmission as a function of frequency was recorded in the specified frequency range. In our analysis we utilized the fact that for plane waves incident normally on a slab of material, resonances occur whenever the slab is an integer number of half wavelengths. Thus, using the sapphire as a substrate, resonances occurred approximately every 50 GHz. Having analyzed the transmission through the sapphire alone prior to mounting the sample, the optical properties of the substrate were well characterized. The index of refraction of mylar was taken to be approximately 1.5, and its extinction coefficient was neglected. Thus using a three-layer transmission model, each resonance was analyzed for the optical properties of the DNA film, allowing for a 1.5 $cm^{-1}$ resolution of the spectrum. Thin tungsten wire grids with a spacing much smaller than the wavelength of our radiation acted as adjustable polarizers to probe the sample anisotropy. Transmission measurements in the UV spectral range were conducted using a Beckman Coulter DU 640 Spectrophotometer.
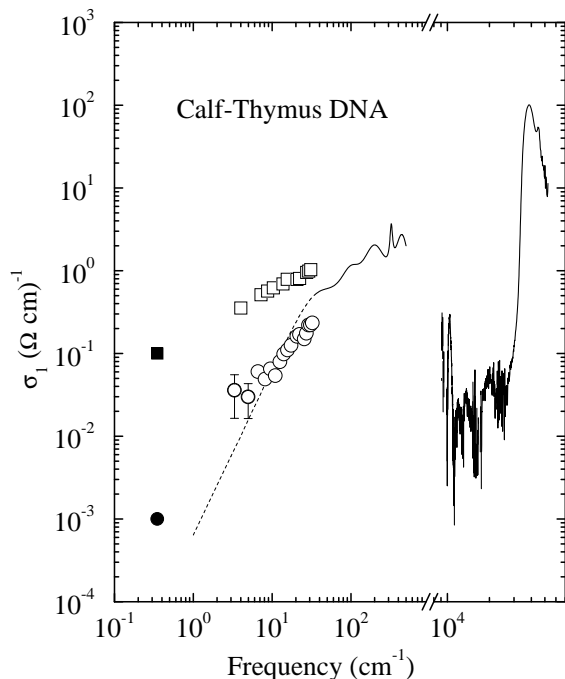


FIG. 1. Frequency dependence of the optical conductivity of calf thymus DNA. Only the conductivity at spectral ranges where electronic excitations occur are displayed. Vibrational modes (arising between 500 and 10,000 $cm^{-1}$) are omitted for clarity.

The optical conductivity, measured over a broad spectral range is displayed in Fig. 1. We have omitted the spectral range between 500 and 10,000 $cm^{-1}$, where various intramolecular vibrational excitations occur, which will be the subject of a separate publication. In the figure we have also displayed the conductivity extracted from the transmission data of Wittlin et al. [13] conducted on dry specimens. Several comments on the experiments we have conducted are in order. First, during experiments with an electric field polarized parallel and perpendicular to the duplex axis we did not observe a substantial anisotropy of the conductivity, and the absorption peaks associated with vibrational modes were also found to be isotropic [13]. While this is surprising, it can be explained by assuming that the DNA duplex while oriented macroscopically does not assume a straight configuration but displays a substantial local directional variation. This has been observed in certain DNA films [14]. As this issue is unresolved, we have not included a factor of $\frac{1}{3}$ in the loss equation; this however does not affect our overall conclusion. Second, it is evident from the figure that data at low frequencies, measured on dry DNA species is reproducible, that is, the conductivity we have evaluated is, within experimental error identical to those found by others [13]. Third, the low frequency optical conductivity depends on the water environment with the conductivity in a wet environment significantly larger than that in a dry environment. We have found similar results earlier for $\lambda$-DNA [8].

The mode with the onset at 30,000 $cm^{-1}$ is due to intra-base electronic excitations associated with the $\pi \to \pi^*$ molecular orbital transitions. This we have confirmed by conducting optical absorption measurements on the individual A, T, C and G bases; the absorption as shown in Fig. 1 is virtually identical to the sum of the optical transitions associated with the four base pair species. The spectral weight

$$\int \sigma(\omega)\, d\omega = \frac{\pi N e^2}{2m} \qquad (1)$$

of the mode, where $N$ is the concentration of charge carriers, and $m$ is the (electronic) mass, has been evaluated by using the measured extinction coefficient. By a numerical integration of the spectra for samples of known dimensions and concentration of DNA, we obtain a value for the concentration of charge carriers of order $N \sim 10^{21} cm^{-3}$, which compares favorably with the concentration evaluated by assuming that there is one electron per base associated with this transition [15], $N = 2 \times 10^{21} cm^{-3}$.

On the basis of this analysis we conclude that the absorption feature in the UV spectral range represents nearly all the spectral weight associated with the electronic excitations of the base pairs of the DNA duplex. We note that this excitation cannot be associated with the bandgap in the usual sense, as this mode does not represent a transition between the highest occupied and

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lowest unoccupied states associated with the entire electronic structure of the DNA duplex. The reason for this is the following: for a duplex, the optical transition we observe corresponds to a transition between energy levels of the various single bases, i.e. intra-base excitations, while the transition matrix element involving energy levels of different bases (such as A to T or C to G optical transitions) is vanishingly small. The bandgap, on the other hand, corresponds to the energy difference between the top of the HOMO band and the bottom of the LUMO band, with these bands in general corresponding to different bases [5].
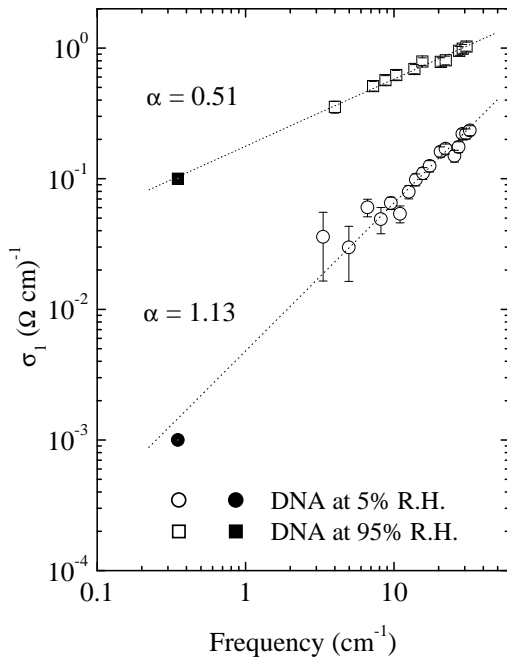


FIG. 2. Frequency dependence of the conductivity of calf thymus DNA in a 5% and a 95% relative humidity environment. The dashed lines are Eq. (2) with the parameters given in the figure.

The optical conductivity below about 500 $cm^{-1}$, represented by the full line in Fig. 1 is due to low frequency vibrations involving the double helix structure. These vibrations have been described earlier [13] and are not discussed here. In Fig. 2 the frequency dependent conductivity, as measured below these vibrational modes in the micro and millimeter wave spectral range is displayed for both dry and fully hydrated DNA. The dashed lines represent a conductivity given by the expression

$$\sigma_1(\omega) = A(T)\omega^\alpha \qquad (2)$$

with the exponent $\alpha$ given in the figure. Such a power law dependence has been observed in a variety of disor-

dered solids, ranging from ionic glasses [14] to materials where the electron states are localized [16]. We believe that contributions to the conductivity due to the counter ions and water molecules, which surround the DNA duplex, can be neglected, and that the conductivity is due to localized electrons or holes, for several reasons. First, both the counter ions and the water in the hydration layers are strongly bound to the (negatively charged) DNA duplex and consequently excitations due to these should occur only at higher frequencies in the infrared spectral range and above. Second, the number of counter ions does not vary during the hydration, and thus they cannot be responsible for the strong increase of the conductivity with the increasing water content. The increased conductivity measured for the hydrated DNA may, in principle, originate from the response of the water molecules surrounding the duplex in the hydration layer. We believe this unlikely as we have measured the dependence of the optical conductivity as a function of humidity, and have found a strongly nonlinear dependence of said conductivity on the number of water molecules surrounding the duplex. Experiments on frozen samples [17] of the same composition, where water molecules and counter-ions are immobilized, show similar behavior indicating that the contribution of the counter-ions to the optical conductivity is negligible. A more likely origin of the difference between the conductivity of the dry and water saturated DNA is as follows. In a water rich or high humidity environment, the DNA duplex takes on a more ordered structure (bases stacked parallel to each other) referred to as its B-form as compared to when the DNA duplex is in a dry or low humidity environment, where the structure is less ordered (bases are stacked with different angles with respect to the main axes of the molecules) and referred to as its A-form. We believe that the increased conductivity is due to the more ordered arrangement of the DNA system in its B-form as compared to the disordered A-form allowing for increased electronic charge transport in spite of the fact that distances between neighboring bases are shorter in the A-form. In Fig. 3 we display the temperature dependence of the conductivity measured at 12, 150 and 500 GHz as a function of temperature. Several features are of importance. First we find a strongly temperature dependent conductivity, and the temperature dependence is typical of a conductivity $\sigma_1$ determined by temperature driven transport processes. Second, the temperature dependence itself depends only weakly on the frequency over a substantial frequency range.

The temperature and frequency dependence of the conductivity as observed at low frequencies has all the hallmarks of a transport process that is determined by transitions between localized electronic states. The frequency dependence of the conductivity under such circumstances is well described by Eq. (2) with the exponent $a$ depending on the conduction process. For instance, in the case of variable range hopping (VRH) the strength of

the electron-electron interactions can change the exponent $a$. For VRH, in the case of non-interacting electrons one finds an approximately linear dependence of the conductivity on frequency whereas in the case of interacting electrons, one finds a quadratic dependence of the conductivity on frequency (plus logarithmic corrections) [18]. We also find a conductivity that is well described by Eq. (2) with exponents different for dry and water saturated DNA. The reason for this difference is not clear; nevertheless the frequency dependence observed is clearly similar to that of a random assembly of charged entities. In the parameter region $k_B T > \hbar \omega$, the prefactor $A(T)$ in Eq. (2), should display a non-exponential temperature dependence. The function $A(T)$ depends on the overall energy scale $E_0$ associated with the localized states. Variable range hopping is the dominant dc conduction mechanism if $E_0 > k_B T$, for which

$$\sigma_{DC} = B \exp\left[ -\left(\frac{T_0}{T}\right)^{\beta} \right] \qquad (3)$$

in one dimension, with $\beta = \frac{1}{2}$, no matter the strength of electron-electron interactions, and the characteristic temperature $T_0$ depending on the localization length and also on the density of states of the carriers. The temperature dependence is non-exponential, and in addition becomes progressively weaker with increasing frequency. The measured temperature dependence displayed in Fig. 3 is in qualitative accordance with such behavior. This then strongly suggests states localized by disorder. Both static disorder associated with the random base pair sequences, and also fluctuations involving the DNA duplex may be responsible [19] for determining the overall temperature and frequency dependence.

Our experimental results, obtained over a broad spectral range strongly suggest that native DNA is a wide bandgap semiconductor, with disorder and counterion fluctuations (among other possible sources) leading to a small number of localized carriers on the base pairs - a situation not unlike what occurs in lightly doped crystalline or amorphous semiconductors or doped polymers [20]. Under such circumstances two important contributions to the optical conductivity emerge: a well defined transition associated with the electron states of the "pure" system (this transition occurring at finite energy) together with a low frequency contribution to the conductivity with prominent frequency and temperature dependencies. We observe both features in native DNA with some modifications from what is found for a typical lightly doped (crystalline or amorphous) semiconductor or polymer. In the latter case one observes a well-defined optical transition between the valence and conduction band, as discussed earlier, for DNA, the transition is between orbitals associated with individual bases. Thus the fact that band structure calculations [5] give a bandgap smaller than that corresponding to the energy for the
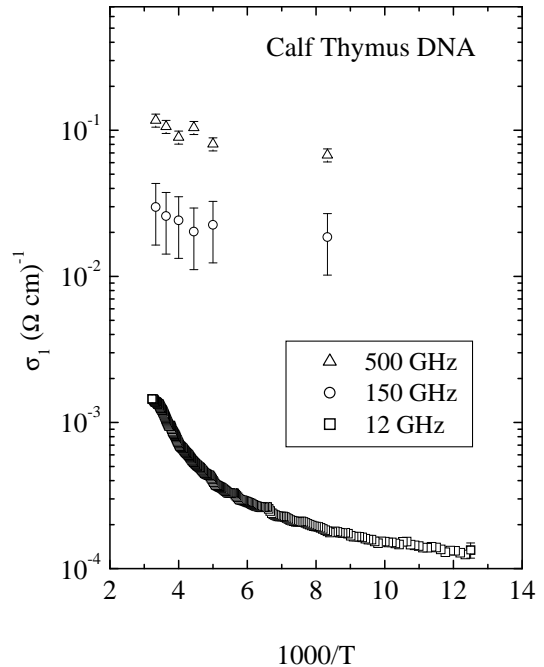


FIG. 3. Temperature dependence of the conductivity of dry calf thymus DNA measured at 12, 100 and 500 GHz.

onset of absorption in Fig. 1 is not surprising.

The number of carriers involved in the low frequency transport process is difficult to estimate as the parameters that enter into the equations for the temperature and frequency dependent conductivity are determined by both the number of carriers, and by the localization length. A comparison with other disordered one-dimensional conductors however allows one to draw some conclusions and to make some order of magnitude estimates. The temperature dependence of the conductivity that we find for DNA is similar to a strongly disordered organic conductor $Qn(TCNQ)_2$ with disorder induced by irradiation [21], for which the localization length is $\xi \sim 10$Å, and the number of carriers is $N \sim 10^{22} cm^{-3}$. The magnitude of the conductivity we find here is approximately three orders of magnitude smaller than that observed in $Qn(TCNQ)_2$. For a conduction process determined by temperature driven transitions between localized electron states, the localization length, $\xi$, mainly determines the overall temperature dependence. The magnitude of $\sigma_1$ reflects both $\xi$ and the number of carriers, $N$. Thus the comparison between calf-thymus DNA and $Qn(TCNQ)_2$ suggests that in native DNA electron states are characterized by a short localization length not exceeding one lattice constant (the distance between base pairs), while the number of carriers participating in the low frequency transport process is of the order

of $N \sim 10^{19} cm^{-3}$. The higher conductivity of DNA in a water rich environment may reflect a different carrier number, but most likely it is due to the more regular B-form of DNA which occurs for high water content, thus also leading to weaker localization effects, and thus to a larger localization length.

The source of the charge entities (electrons or holes) which are associatedwith the low frequency conductivity is not obvious. The random base pair sequences, together with disorder associated with the finite persistence length, and counter ion fluctuations all may lead to a small number of localized charges on the base pair stack. The fact that the states, which contribute to the low frequency optical response, are localized has different ingredients. The random base pair sequences which occur in native DNA lead to a random potential along the duplex, and thus to charge localization. The potential energy fluctuations associated with the base pair sequences are of the order of $0.5eV$, about ten times larger than the overlap integral between the electron states on neighboring base pairs along the double helix [19,22]. Under such circumstances the localization length is of the order of one lattice constant, comparable to the value we inferred before. One should also note that equally important is the dynamic disorder associated with base pair fluctuations, of which the influence on charge transport along the DNA duplex has been conjectured earlier [19].

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